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14. ABSTRACT Through various environments a factor influencing AP chemical activity is the propensity of coarse AP to produce porosity formation within its crystals. Porosity formation in coarse AP seems similar although at differing rates due to pressure and temperature influences in both isolated crystals and solid propellant combustions. Consolidated coarse AP crystals appear to be chemically unstable so that pure consolidated crystals cannot be made. Natural and accumulated trace impurities are responsible for observed porosity formation. In combustion environments kinetic action rates for coarse AP can be altered by materials on crystal surfaces and within the crystal bodies. Since orthorhombic crystal AP reaction rates are much faster in combustion environments than cubic crystal AP, orthorhombic phase AP is a primary actor during combustions. At very high pressures AP self combustion exhibits differential recession rates depending on whether surface regression is normal or transverse to the principal axis of its orthorhombic crystal structure. This behavior might be described as biaxial burning. Coarse AP oxidizer has observable chemical interactions that have not been observed for fine AP oxidizer during thermal decomposition and combustion environments. Coarse AP oxidizer has widely different chemical kinetic reaction rates between low and high heat fluxes. Widely different reaction rates are also observed between low and high pressure confinements. In solid propellants coarse AP promotes dark zone combustion, low burn rate pressure exponent, ease of burn rate adjustment, burn rate pressure exponent slope break, and slow cookoff violence.					
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Peculiar Traits of Coarse AP

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AFRL/RQRP, Edwards Rocket Site, CA

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Objectives

Global view of AP large crystal reactivity

AP in decompositions, self-combustion, & propellants



Coarse AP seems an individual chemical

Coarse AP combustions differ from fine and porous AP

Orthorhombic phase is most reactive



It's all about the gremlins in coarse AP

Microscopic active centers origin

Bircumshaw and Newman

Active center traits

Raevskii, Manelis, Boldyrev, Khairtdinov

Orthorhombic AP crystal burning

Thom L. Boggs



AP Combustions and Active Centers

Coarse AP in reduced smoke propellant

Richard M. Miller

Exponent shifts

Slow cookoff

Erosive burning

Dan Meyer



Active centers in coarse AP

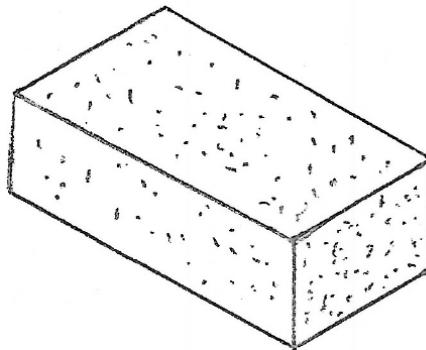
Bircumshaw, Newman

Active centers are sources of AP decomposition gases

AP low temperature decomposition (LTD)

Most unstable AP particles ~100 to 200 μ size

Impure AP has shorter induction periods





Coarse AP active center traits

Raevskii, Manelis

Grow to maximum size of $\sim 2\mu$

Have non-uniform distribution

Active site numbers multiplied by impurities

Density of pores estimated as being up to $10^6/\text{cm}^2$



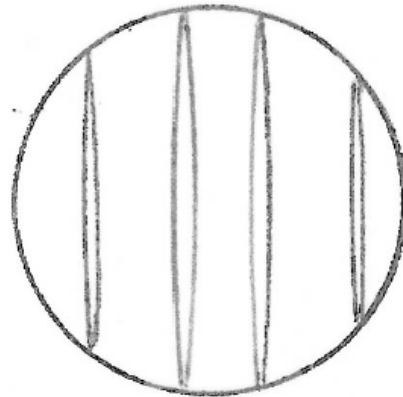
Coarse AP active center traits 2

Raevskii, Manelis

Holes produced were called elipsoids of revolution

Active centers are sub-surface by 3 μ or more

Active center internal pressures are ~20 atmospheres





Coarse AP active center traits 3

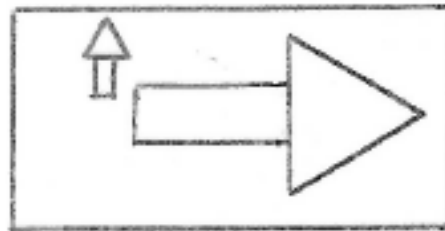
Raevskii, etal

Active sites in coarse AP move in multiple directions

Smaller centers called “germs” coalesce up to maximum size of 2 μ

Movement quicker along major orthorhombic axis, $E_a = 31$ kcal

Transverse movement, $E_a = 33$ kcal





Active center chemistry

Khairtdinov and Boldyrev

Active sites contain chlorate ion and AP decomposition products

Chlorate content increases LTD rates; shortens induction periods

Gassing activation for high purity AP, $E_a = 70$ kcal

Activation for impure AP (~99%), $E_a = 50$ kcal



Active center chemistry 2

Khairtdinov and Boldyrev

AP crystal impurities greatly multiply active centers

Coarse AP cannot be made completely pure

No AP LTD with 5 micron AP



Active center chemistry 3

Boldyrev

Perchlorate ions are nonrotating in orthorhombic AP

***Chlorate ion movement cannot push aside perchlorate ions**

***Chlorate ions can migrate by oxygen atom swapping
with adjacent perchlorate ions**



AP Self Combustion

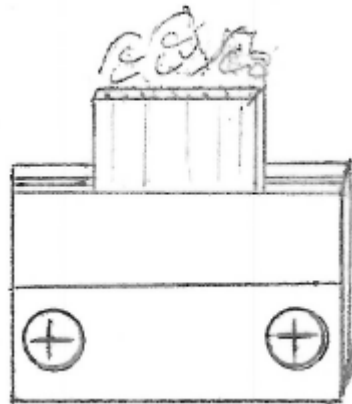
Thom L. Boggs

Cleaved platelets of AP crystals burned from 300 to 6200 psi

Copper vise mount heat absorption provided flame quenching

At low pressures AP recession was uniform with bubbling

AP cubic phase participation was minimal during burning





AP Self Combustion 2

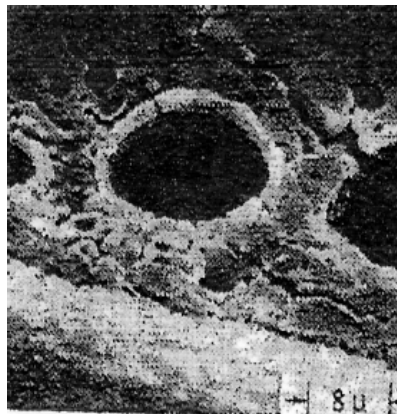
Thom L. Boggs

Identified 4 pressure zones based upon exponent behavior

Up to 800 psi burning showed agitated, frothing material

Up to 2000 psi a few large craters were observed

Froth disappeared as pressures were raised toward 2000 psi





AP Self Combustion 3

Thom L. Boggs

Parallel ridges and valley surfaces seen at 1000 to 1500 psi

Isolated AP vertical needle pockets at 1500 and 1800 psi

Negative exponents, bouncing flamlets between 2000 to 4000 psi

Extremely irregular AP surface regression

Hightower and Price





AP Self Combustion 4

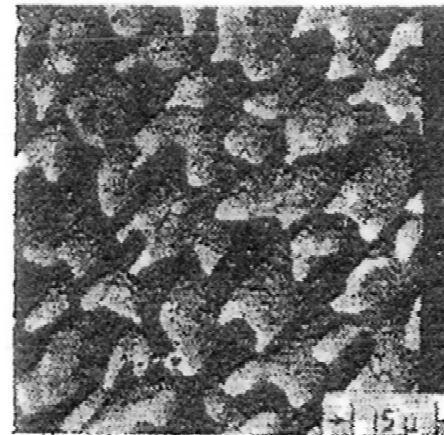
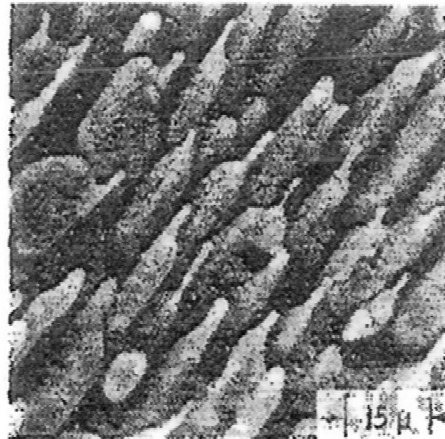
Thom L. Boggs

Above 4000 psi AP regressed uniformly

Quenched AP surface had irregular AP needles

***AP needles seemed from partial tubelike, curved surfaces**

Boggs



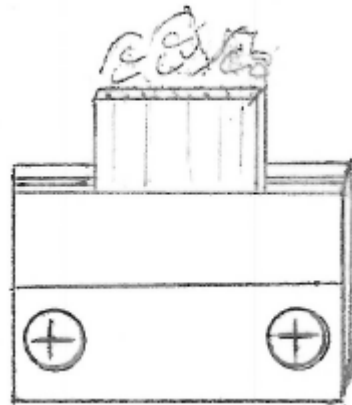


AP Burn Discussion

Was Boggs' bubbling from AP mist supported by vertical gas jetlets from active centers?

Did Boggs burn a few samples at 1000 to 2000 psi with orthorhombic main axis normal to regressing surface?

How can AP needles be formed? Bidirectional recession?





Combustion bomb trials

Richard M. Miller

Reduced smoke HTPB propellant, 200/2 microns

Several millisecond time delay before coarse AP ejection

***Coarse AP particle flame retardancy**





Combustion bomb trials 2

AP phase change may enable coarse particle breakage

Fractured coarse AP ejection agrees with dark zone

Time delay before coarse AP ejection may cause low exponent



Porous AP in solid propellant

Edwin L. Lista, China Lake

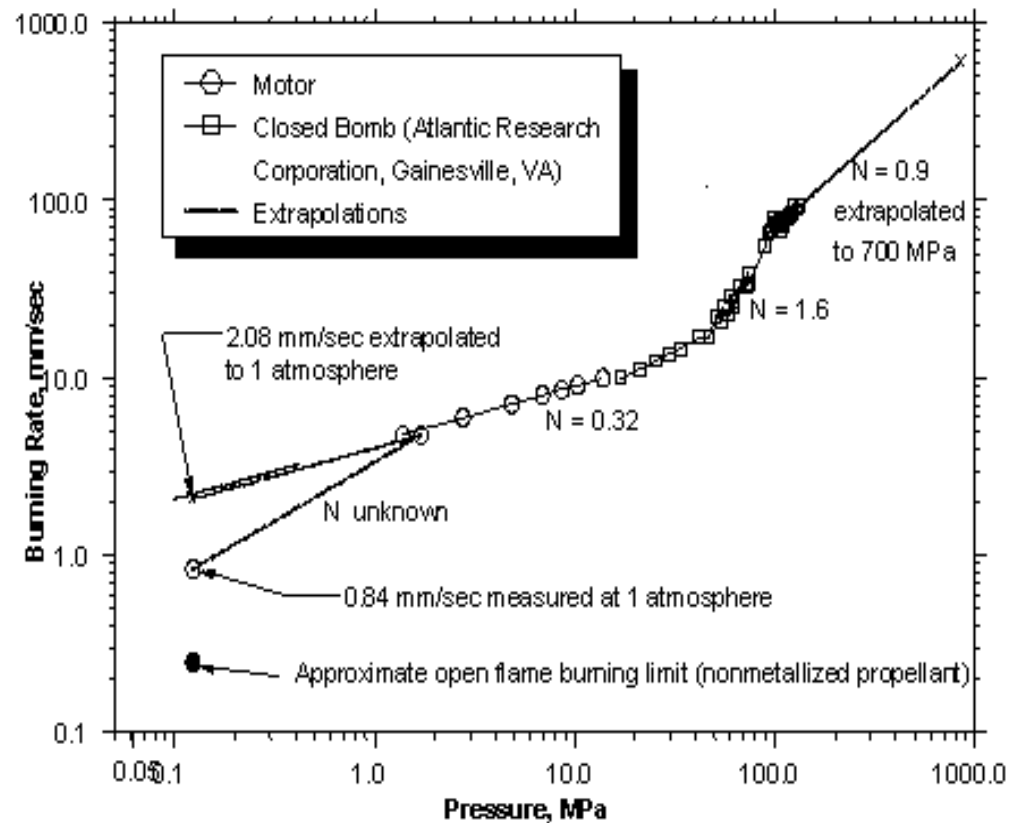
Demonstrated 3.5 ips @ 2000

Burn rate pressure exponents were 0.6

Low densities and erratic burn rates not suitable for systems



Coarse AP propellant exponent slope break





Coarse AP propellant exponent slope break 2

Slope break thresholds inversely related to AP particle size

With 90 micron coarse AP no slope break observed to 60k psi

**Pressure exponent threshold shifted marginally as 200
micron AP content reduced to 5%**

Ready gains in burn rate by using smaller coarse oxidizer



AP LTD drive combustion slope breaks

**Propellant slope break behavior similar to Boggs'
data above 4000 psi**

**Minimization of induction period may transfer fire through
coarse AP faster than normal binder regression**



Coarse AP LTD gives higher burn w/pressure

Increasing proportion of abruptly triggered coarse AP particles continues to increase burn rate

AP LTD process became saturated at about 12,500 psi



Motor slow cookoffs with coarse AP oxidizer

Slow heating rate provides high temperature duration

AP decomposition gases and porosity provide void volumes

Organic components can provide AP-organic molecular association



Coarse AP active sites influence erosive burning

High purity coarse AP LTD has activation energy = 70 kcal

99% purity coarse AP LTD has activation energy = 50 kcal

Low purity AP should provide faster propellant erosion rates

Dan Meyer has data about AP purity and erosion rates



Summary, coarse AP active centers

Coarse AP never 100% pure

Crystalline AP contains small active centers

Active centers move by directional preference

Center movements may be oxygen atom swapping



Summary, coarse AP active centers 2

When initiated, active centers cause ellipsoid pores

Pore emissions may have levitated AP powder

Activation energies for pore emissions vary

Hi pressure AP needle residues indicate bidirectional burns



Summary, coarse AP active centers 3

Subsurface active centers may cause induction periods

Induction periods seen in coarse AP ejections

Coarse AP ejections may be primary combustion mode

AP ejections support dark zones



Summary, coarse AP active centers 4

Ejection delays may promote low exponents

Exponent slope break due to minimal induction period?

Loss of AP crystal structure suggests slow cookoff violence

Low purity AP should enhance propellant erosive burning